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(54) Title: STABLE PHASE CHANGE MATERIALS FOR USE IN TEMPERATURE REGULATING SYNTHETIC FIBERS,
FABRICS AND TEXTILES

(57) Abstract: A stabilized phase change composition comprises a phase change material and a stabilizing agent selected from the group consisting of antioxidants and thermal stabilizers. The stabilizing agent provides oxidative or thermal stabilizing to the phase change material. The stabilized phase change composition may be used or incorporated in a variety of process (e.g., melt spinning processes, extrusion processes, injection molding processes, and so forth) to form articles having enhanced reversible thermal properties. Exemplary articles that may be formed include, by way of example and not by limitation, synthetic fibers (e.g., nylon fibers, polyester fibers, polyethylene fibers, polypropylene fibers, and multi-component fibers), fabric materials, textiles, films, foams, sheets, pellets, rods, and injection molded articles.

**STABLE PHASE CHANGE MATERIALS FOR USE IN TEMPERATURE
REGULATING SYNTHETIC FIBERS, FABRICS AND TEXTILES**

FIELD OF THE INVENTION

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The present invention relates generally to phase change materials. More particularly, the present invention relates to stabilized phase change materials and methods of stabilizing phase change materials that are useful in the manufacture of melt spun synthetic fibers.

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BACKGROUND OF THE INVENTION

Many fabric materials are made from synthetic fibers. While the spirit and scope of this invention is not to be limited to the following definition, a fiber is typically considered to have a length several times (e.g., 100 times or more) greater than its diameter.

15 Conventionally, two processes are used to manufacture synthetic fibers: a wet solution process and a melt spinning process. The wet solution process is generally used to form acrylic fibers, while the melt spinning process is generally used to form nylon fibers, polyester fibers, polypropylene fibers, and other similar type fibers. As is well known, a 20 nylon fiber comprises a long-chain synthetic polyamide polymer characterized by the presence of an amide group -CONH-, a polyester fiber comprises a long-chain synthetic polymer having at least 85 percent by weight of an ester of a substituted aromatic carboxylic acid unit, and a polypropylene fiber comprises a long-chain synthetic crystalline polymer having at least 85 percent by weight of an olefin unit and typically having a molecular 25 weight of about 40,000 or more.

The melt spinning process is of particular interest since a large portion of the synthetic fibers that are used in the textile industry are manufactured by this technique. The melt spinning process generally involves passing a melted polymeric material through a device that is known as a spinneret to thereby form a plurality of individual synthetic fibers. 30 Once formed, the synthetic fibers may be collected into a strand or made into a cut staple. The synthetic fibers can be used to make woven or non-woven fabric materials, or alternatively, the synthetic fibers can be wound into a yarn to be used thereafter in a weaving or a knitting process to form a synthetic fabric material.

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Phase change materials have been incorporated into acrylic fibers to provide enhanced reversible thermal properties to the fibers themselves as well as to fabric materials made therefrom. This is readily accomplished, in part due to the high levels of volatile materials (e.g., solvents) typically associated with the wet solution process of forming acrylic fibers. However, it is more problematic to incorporate phase change materials into melt spun synthetic fibers. During a melt spinning process, temperatures involved are typically in the range of from about 200°C to about 380°C, and pressures encountered may be as high as 3000 pounds per square inch. Such processing conditions may induce degradation of the phase change materials and thus may lead to inadequate levels of thermal regulating properties normally associated with use of the phase change materials.

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At elevated temperatures or pressures, certain phase change materials such as, for example, paraffinic hydrocarbons and waxes may undergo thermally induced decomposition or isomerization. Factors affecting the extent and nature of thermally induced decomposition and isomerization include magnitude of temperature, pressure, and duration of time during which a phase change material is subjected to elevated temperatures or pressures. For paraffinic hydrocarbons at a temperature of about 350°C, thermally induced decomposition may lead to formation of lower molecular weight products (e.g., gaseous products), and thermally induced isomerization may lead to formation of branched-chain alkanes. Accordingly, a lesser amount of an unreacted paraffinic hydrocarbon may remain to effectively provide a thermal regulating property. Moreover, products resulting from thermally induced decomposition or isomerization may act as impurities. For example, a magnitude of a paraffinic hydrocarbon's latent heat of fusion may depend on the purity of the paraffinic hydrocarbon and on the ability of the paraffinic hydrocarbon to crystallize fully. Impurities resulting from thermally induced decomposition or isomerization may hinder crystallization of a remaining unreacted paraffinic hydrocarbon to further reduce its effectiveness.

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Alternatively or in conjunction with thermally induced decomposition or isomerization, certain phase change materials may undergo oxidation at elevated temperatures or pressures. For example, paraffinic hydrocarbons may undergo significant oxidation in the presence of atmospheric oxygen at temperatures as low as about 80°C to about 120°C. Oxidation may lead to a lesser amount of an unreacted phase change material remaining to effectively provide a thermal regulating property. Moreover, products resulting from oxidation of the phase change material may act as impurities to further

reduce effectiveness of the phase change material. For example, oxidation of paraffinic hydrocarbons may lead to formation of organic products such as, for example, esters, alcohols, aldehydes, acids, peroxides, or water. The presence of impurities can lower the latent heat and adversely affect a thermal regulating property provided by a phase change material and by a synthetic fiber or fabric material in which the phase change material is incorporated.

When a phase change material is degraded as a result of elevated temperatures or pressures, the melt spinning process itself can be adversely affected. In particular, products resulting from thermally induced decomposition, thermally induced isomerization, or oxidation of the phase change material may react with a fiber-grade thermoplastic polymer and lead to degradation (e.g., weakening or discoloration) of the polymer itself and of a resulting synthetic fiber.

It is against this background that a need arose to develop stabilized phase change materials that would be useful in the manufacture of melt spun synthetic fibers.

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SUMMARY OF THE INVENTION

In one innovative aspect, the present invention relates to a stabilized phase change composition. In one exemplary embodiment, the stabilized phase change composition may comprise a phase change material and a stabilizing agent selected from the group consisting of antioxidants and thermal stabilizers.

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In another innovative aspect, the present invention relates to an encapsulated phase change material. In one exemplary embodiment, the encapsulated phase change material may comprise a hollow shell defining an internal cavity and a phase change composition positioned in the internal cavity, wherein the phase change composition comprises a phase change material and a stabilizing agent selected from the group consisting of antioxidants and thermal stabilizers.

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In another exemplary embodiment, the encapsulated phase change material may comprise a hollow shell defining an internal cavity, wherein the hollow shell comprises a base material and a stabilizing agent dispersed within the base material, and the stabilizing agent is selected from the group consisting of antioxidants and thermal stabilizers. The encapsulated phase change material may further comprise a phase change material positioned in the internal cavity.

BRIEF DESCRIPTION OF THE DRAWINGS

5 For a better understanding of the nature and objects of the invention, reference should be made to the following detailed description taken in conjunction with the accompanying drawings, in which:

FIG. 1 illustrates an enlarged cross sectional view of an exemplary embodiment of an encapsulated phase change material; and

10 FIG. 2 illustrates an enlarged cross sectional view of another exemplary embodiment of an encapsulated phase change material.

DETAILED DESCRIPTION

The present invention relates to stabilized phase change materials and methods of stabilizing phase change materials. More particularly, embodiments of the invention provide for the oxidative stabilization and thermal stabilization of phase change materials. Oxidative stabilization may be provided through use of one or more antioxidants, while thermal stabilization may be provided through use of one or more thermal stabilizers. The stabilized phase change materials and stabilization methods in accordance with various embodiments of the invention may be used or incorporated in a variety of processes (e.g., melt spinning processes, extrusion processes, injection molding processes, and so forth) to form articles having enhanced reversible thermal properties. Embodiments of the invention offer a degree of protection to the phase change materials from elevated temperatures or pressures to form a variety of articles, such as, by way of example and not by limitation, 15 synthetic fibers (e.g., nylon fibers, polyester fibers, polyethylene fibers, polypropylene fibers, and multi-component fibers), fabric materials, textiles, films, foams, sheets, pellets, 20 granules, rods, and injection molded articles.

25 In general, a phase change material may comprise any substance (or mixture of substances) that has the capability of absorbing or releasing thermal energy to reduce or eliminate heat flow at or within a temperature stabilizing range. The temperature stabilizing range may comprise a particular transition temperature or range of transition temperatures. A phase change material used in conjunction with various embodiments of the invention 30 preferably will be capable of inhibiting a flow of thermal energy during a time when the

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phase change material is absorbing or releasing heat, typically as the phase change material undergoes a transition between two states (e.g., liquid and solid states, liquid and gaseous states, solid and gaseous states, or two solid states). This action is typically transient, e.g., will occur until a latent heat of the phase change material is absorbed or released during a heating or cooling process. Thermal energy may be stored or removed from the phase change material, and the phase change material typically can be effectively recharged by a source of heat or cold.

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According to some embodiments of the invention, a phase change material may be a solid/solid phase change material. A solid/solid phase change material is a type of phase change material that typically undergoes a transition between two solid states (e.g., a crystalline or mesocrystalline phase transformation) and hence typically does not become a liquid during use.

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Phase change materials that can benefit from stabilization in accordance with various embodiments of the invention include a variety of organic substances. Exemplary phase change materials include, by way of example and not by limitation, hydrocarbons (e.g., straight chain alkanes or paraffinic hydrocarbons, branched-chain alkanes, unsaturated hydrocarbons, halogenated hydrocarbons, and alicyclic hydrocarbons), waxes, oils, fatty acids, fatty acid esters, dibasic acids, dibasic esters, 1-halides, primary alcohols, aromatic compounds, anhydrides (e.g., stearic anhydride), ethylene carbonate, polyhydric alcohols (e.g., 2,2-dimethyl-1,3-propanediol, 2-hydroxymethyl-2-methyl-1,3-propanediol, ethylene glycol, polyethylene glycol, pentaerythritol, dipentaerythritol, pentaglycerine, tetramethylol ethane, neopentyl glycol, tetramethylol propane, monoaminopentaerythritol, diaminopentaerythritol, and tris(hydroxymethyl)acetic acid), polymers (e.g., polyethylene, polyethylene glycol, polypropylene, polypropylene glycol, polytetramethylene glycol, and copolymers, such as polyacrylate or poly(meth)acrylate with alkyl hydrocarbon side chain or with polyethylene glycol side chain and copolymers comprising polyethylene, polyethylene glycol, polypropylene, polypropylene glycol, or polytetramethylene glycol), and mixtures thereof.

Table 1 provides a list of exemplary paraffinic hydrocarbons that may be used as the phase change material stabilized in the accordance with various embodiments of the invention.

Table 1

Paraffinic Hydrocarbon	No. of Carbon Atoms	Melting Point °C
n-Octacosane	28	61.4
n-Heptacosane	27	59.0
n-Hexacosane	26	56.4
n-Pentacosane	25	53.7
n-Tetracosane	24	50.9
n-Tricosane	23	47.6
n-Docosane	22	44.4
n-Heneicosane	21	40.5
n-Eicosane	20	36.8
n-Nonadecane	19	32.1
n-Octadecane	18	28.2
n-Heptadecane	17	22.0
n-Hexadecane	16	18.2
n-Pentadecane	15	10.0
n-Tetradecane	14	5.9
n-Tridecane	13	-5.5

5 A phase change material can be a mixture of two or more substances (e.g., two or more of the exemplary phase change materials discussed above). By selecting two or more different substances (e.g., two different paraffinic hydrocarbons) and forming a mixture thereof, a temperature stabilizing range can be adjusted over a wide range for any desired application. According to some embodiments of the invention, a phase change material may comprise a copolymer of two or more substances (e.g., two or more of the exemplary phase change materials discussed above).

10 Phase change materials that can benefit from stabilization in accordance with the invention may include phase change materials in a non-encapsulated form and phase change materials in an encapsulated form. A phase change material in a non-encapsulated form may be provided as a solid in a variety of forms (e.g., bulk form, powders, pellets, granules,

flakes, and so forth) or as a liquid in a variety of forms (e.g., molten form, dissolved in a solvent, and so forth).

5 In general, an antioxidant used in conjunction with various embodiments of the invention may comprise any substance (or mixture of substances) that has the capability of preventing or retarding oxidation of a substance (or mixture of substances) to be stabilized (e.g., a phase change material). According to some embodiments of the invention, an antioxidant has the capability of preventing or retarding oxidation of a phase change material in the presence of oxygen (e.g., atmospheric oxygen) or in the presence of oxygen free radicals at temperatures and pressures encountered in processes such as, for example, 10 melt spinning processes, extrusion processes, or injection molding processes. In particular, an antioxidant in accordance with an embodiment of the invention may prevent or retard formation of products resulting from reaction of the phase change material with oxygen or with oxygen free radicals, which products may include, for example, esters, alcohols, aldehydes, acids, peroxides, or water. Typically, an antioxidant may be selected to be 15 compatible with (e.g., low chemical reactivity with respect to) a phase change material to be stabilized.

Exemplary antioxidants that may be used in accordance with various embodiments of the invention include phenolic antioxidants (i.e., antioxidants comprising a benzene ring attached to one or more hydroxy groups -OH) such as, by way of example and not by 20 limitation, octadecyl-3-(3,5-di-tert butyl-4-hydroxyphenyl) propionate; 2,6-di-tert-butyl-p-cresol; 2,6-diphenyl-4-octadecyloxyphenol; stearyl-(3,5-dimethyl-4-hydroxybenzyl) thioglycolate; stearyl-beta-(4-hydroxy-3,5-di-tert-butylphenyl) propionate; distearyl-3,5-di-tert-butyl-4-hydroxybenzyl phosphate; 2,4,6-tris(3',5'-di-tert-butyl-4'-hydroxybenzylthio)-25 1,3,5-triazine; distearyl(4-hydroxy-3-methyl-5-tert-butyl) benzylmalonate; 2,2'-methylenebis(4-methyl-6-tert-butylphenol); 4,4'-methylenebismethylenebis(2,6-di-tert-butylphenol); 2,2'-methylenebis[6-(1-methylcyclohexyl)p-cresol]; bis[3,5-bis(4-hydroxy-3-tert-butylphenyl)butyric acid] glycol ester; 4,4'-butyldenebis(6-tert-butyl-m-cresol); 2,2'-ethylidenebis(4,6-di-tert-butylphenol); 2,2'-ethylidenebis(4-sec-butyl-6-sec-butylphenol); 30 1,1,3-tris(2-methyl-4-hydroxy-5-tert-butylphenyl)butane; bis[2-tert-butyl-4-methyl-6-(2-hydroxy-3-tert-butyl-5-methylbenzyl-phenyl] terephthalate; 1,3,5-tris(2,6-dimethyl-3-hydroxy-4-tert-butylbenzyl) isocyanurate; 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene; tetrakis[methylene-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate]methane; 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)

isocyanurate; 1,3,5-tris[(3,5-di-tert-butyl-4-hydroxyphenyl)propionyloxyethyl] isocyanurate; 2-octylthio-4,6-di(4-hydroxy-3,5-di-tert-butyl)phenoxy-1,3,5-triazine; 4,4'-thiobis(6-tert-butyl-m-cresol); 2,2'-thiobis(6-t-butyl-4-methylphenol); 2,2'-thiobis(4-octylphenol); 4,4'-thiobis(6-t-butyl-3-methylphenol); 4,4'-thiobis(6-t-butyl-2-methylphenol); phenolic polymers; and mixtures thereof.

It should be recognized that phenolic antioxidants may include sterically hindered phenolic antioxidants, according to some embodiments of the invention. As one of ordinary skill in the art will understand, the term "sterically hindered" is typically understood to refer to an arrangement of atoms of a molecule such that its reactivity with respect to another molecule may be prevented or retarded. A desirable sterically hindered phenolic antioxidant according to an embodiment of the invention is octadecyl-3-(3,5-di-tert butyl-4-hydroxyphenyl) propionate, which is available under the trade name IRGANOX 1076 from Ciba Specialty Chemicals, Inc.

Other exemplary antioxidants include thioether antioxidants (i.e., antioxidants comprising a sulfide group -S-) such as, by way of example and not by limitation, thioether antioxidants comprising polyhydric alcohol esters of dialkyl thiodipropionate (e.g., dilauryl thiodipropionate, dimyristyl thiodipropionate, distearyl thiodipropionate, and so forth) and alkyl thiopropionate (e.g., butyl thiopropionate, octyl thiopropionate, lauryl thiopropionate, stearyl thiopropionate, and so forth). Exemplary polyhydric alcohols include, by way of example and not by limitation, ethylene glycol, polyethylene glycol, pentaerythritol, dipentaerythrital, pentaglycerine, tetramethylol ethane, neopentyl glycol, tetramethylol propane, monoaminopentaerythritol, diaminopentaerythritol, and tris(hydroxymethyl)acetic acid.

In general, a thermal stabilizer used in accordance with various embodiments of the invention may comprise any substance (or mixture of substances) that has the capability of preventing or retarding thermally induced decomposition or isomerization of a substance (or mixture of substances) to be stabilized (e.g., a phase change material). According to some embodiments of the invention, a thermal stabilizer has the capability of preventing or retarding thermally induced decomposition or isomerization of a phase change material at temperatures and pressures encountered in processes such as, for example, melt spinning processes, extrusion processes, or injection molding processes. In particular, a thermal stabilizer in accordance with an embodiment of the invention may prevent or retard formation of lower molecular weight products or isomers resulting from thermally induced

decomposition or isomerization of the phase change material. Typically, a thermal stabilizer may be selected to be compatible with (e.g., low chemical reactivity with respect to) a phase change material to be stabilized.

Exemplary thermal stabilizers that may be used in accordance with various 5 embodiments of the invention include organic substances comprising phosphorus (e.g., phosphites (i.e., organic substances comprising a phosphorus atom attached to three oxygen atoms by single bonds, respectively), phosphonites (i.e., organic substances comprising a phosphorus atom attached to two oxygen atoms and one carbon atom by single bonds, respectively), and so forth) such as, by way of example and not by limitation, 10 trisnonylphenyl phosphite; tridecyl phosphite; octyl diphenyl phosphite; tris(2,4-di-tert-butylphenyl) phosphite; triphenyl phosphite; tris(mono, di-mixed nonylphenyl) phosphite; distearyl pentaerythritol diphosphite; hexa(tridecyl)-1,1,3-tris(2-methyl-5-tert-butyl-4-hydroxyphenyl)butane triphosphite; tetra(C_{sub}.12-15 mixed alkyl)-4,4'-isopropylidene 15 diphenyl diphosphite; tetra(tridecyl)-4,4'-butylidenebis(3-methyl-6-tert-butylphenol) diphosphite; bis(octylphenyl).bis[4,4'-butylidenebis(3-methyl-6-tert-butylphenol)].1,6-hexanediol diphosphite; phenyl.4,4'-isopropylidenediphenol.pentaerythritol diphosphite; 20 bis(2,4-di-tert-butylphenyl)pentaerythritol diphosphite; di(nonylphenyl)pentaerythritol diphosphite; 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide; tetrakis-(2,4-di-tert-butylphenyl)-4,4'-biphenylene diphosphite, 3,9-di(2,4-di-tert-butylphenoxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane; tetrakis(2,4-di-tert-butylphenyl)-4,4'-bis(diphenylene) phosphonite; tetrakis(2,4-di-tert-butylphenyl)4,4'-biphenylene 25 diphosphonite; and mixtures thereof.

According to an embodiment of the invention, a thermal stabilizer used is desirably trisnonylphenyl phosphite (molecular formula: C₄₅H₆₉O₃P), which is available under the 25 trade name Weston TNPP Phosphite from GE Specialty Chemicals, Inc.

Certain embodiments of the invention relate to a stabilized phase change composition. According to some embodiments of the invention, the phase change composition may comprise a phase change material and one or more stabilizing agents. A stabilizing agent may be an antioxidant or a thermal stabilizer, according to some 30 embodiments of the invention.

The phase change composition may comprise from about 0.01 percent to about 10 percent by weight of a stabilizing agent and from about 90 percent to about 99.99 percent by weight of the phase change material, according to some embodiments of the invention.

According to an embodiment of the invention, the phase change composition typically comprises from about 0.02 percent to about 1 percent by weight of a stabilizing agent.

It should be recognized that two or more stabilizing agents may be included in the phase composition according to some embodiments of the invention, and the stabilizing agents may differ from each other in some fashion. For instance, the phase change composition may comprise an antioxidant and a thermal stabilizer, two different antioxidants, or two different thermal stabilizers. According to some embodiments of the invention, the phase change composition may comprise from about 0.01 percent to about 10 percent by weight and typically from about 0.02 percent to about 1 percent by weight of the two or more stabilizing agents taken collectively. According to other embodiments of the invention, the phase change composition may comprise from about 0.01 percent to about 10 percent by weight and typically from about 0.02 percent to about 1 percent by weight of each of the two or more stabilizing agents.

In forming the phase change composition, one or more stabilizing agents may be incorporated during a wet flushing step of forming the phase change material. Alternatively or in conjunction, one or more stabilizing agents may be added to, mixed with, or dispersed in the phase change material in a non-encapsulated form to form the phase change composition. For instance, one or more stabilizing agents may be dry blended with the phase change material in a solid form or dispersed in the phase change material in a liquid form. Depending on the method used to form the phase change composition and other factors (e.g., miscibility or solubility of the one or more stabilizing agents in the phase change material), the phase change composition may be provided as, by way of example and not by limitation, a solid mixture, a liquid mixture, a suspension, a solution, or other forms.

Once formed, the stabilized phase change composition may be used in melt spinning processes, extrusion processes, or injection molding processes to form a variety of articles having enhanced reversible thermal properties. According to some embodiments of the invention, the phase change composition may be mixed with one or more polymeric materials to form a blend, such as by dispersing the phase change composition in a melt of the one or more polymeric materials. In general, a polymeric material used to form the blend may comprise any polymer (or mixture of polymers). Typically, a polymeric material comprises a thermoplastic polymer (or mixture of thermoplastic polymers) (i.e., one that can be heated to form a melt and subsequently shaped or molded to form an article). According

to some embodiments of the invention, a polymeric material may be selected to be compatible with or to have an affinity for the phase change composition. Alternatively or in conjunction, the polymeric material may be selected to provide one or more desired physical properties for an article to be formed (e.g., a synthetic fiber).

Exemplary polymeric materials include, by way of example and not by limitation, polyamides (e.g., Nylon 6, Nylon 6/6, Nylon 12, polyaspartic acid, polyglutamic acid, and so forth), polyamines, polyimides, polyacrylics (e.g., polyacrylamide, polyacrylonitrile, esters of methacrylic acid and acrylic acid, and so forth), polycarbonates (e.g., polybisphenol A carbonate, polypropylene carbonate, and so forth), polydienes (e.g., 5 polybutadiene, polyisoprene, polynorbornene, and so forth), polyepoxides, polyesters (e.g., polyethylene terephthalate, polybutylene terephthalate, polytrimethylene terephthalate, polycaprolactone, polyglycolide, polylactide, polyhydroxybutyrate, polyhydroxyvalerate, polyethylene adipate, polybutylene adipate, polypropylene succinate, and so forth), polyethers (e.g., polyethylene glycol (polyethylene oxide), polybutylene glycol, 10 polypropylene oxide, polyoxymethylene (paraformaldehyde), polytetramethylene ether (polytetrahydrofuran), polyepichlorohydrin, and so forth), polyflourocarbons, formaldehyde polymers (e.g., urea-formaldehyde, melamine-formaldehyde, phenol formaldehyde, and so forth), natural polymers (e.g., cellulosics, chitosans, lignins, waxes, and so forth), polyolefins (e.g., polyethylene, polypropylene, polybutylene, polybutene, polyoctene, and so forth), polyphenylenes (e.g., polyphenylene oxide, polyphenylene sulfide, polyphenylene 15 ether sulfone, and so forth), silicon containing polymers (e.g., polydimethyl siloxane, polycarbomethyl silane, and so forth), polyurethanes, polyvinyls (e.g., polyvinyl butyral, polyvinyl alcohol, polyvinyl acetate, polystyrene, polymethylstyrene, polyvinyl chloride, polyvinyl pyrrolidone, polymethyl vinyl ether, polyethyl vinyl ether, polyvinyl methyl 20 ketone, and so forth), polyacetals, polyarylates, copolymers (e.g., polyethylene-co-vinyl acetate, polyethylene-co-acrylic acid, polybutylene terphthalate-co-polytetramethylene terephthalate, polylauryllactam-block-polytetrahydrofuran, and so forth), and mixtures 25 thereof.

It should be recognized that a stabilizing agent comprising the phase change composition may provide oxidative or thermal stabilization not just to the phase change material but also to the one or more polymeric materials comprising the blend, according to some embodiments of the invention. Also, one or more additional stabilizing agents may be added when forming the blend to provide additional oxidative or thermal stabilization to 30

either or both the phase change material and the one or more polymeric materials. The one or more additional stabilizing agents may be the same as or different from the one or more stabilizing agents comprising the phase change composition. The resulting blend may then be processed to form, by way of example and not by limitation, synthetic fibers (e.g., nylon fibers, polyester fibers, polyethylene fibers, polypropylene fibers, and multi-component fibers), films, foams, sheets, pellets, granules, rods, and injection molded articles.

It should be further recognized that the phase change composition may be encapsulated, according to some embodiments of the invention. In particular, additional embodiments of the invention relate to a stabilized encapsulated phase change material. With reference to FIG. 1, an enlarged cross sectional view of an exemplary embodiment of an encapsulated phase change material 100 is illustrated. The encapsulated phase change material 100 comprises a hollow shell 102 defining an internal cavity 104, and a phase change material is enclosed and positioned in the internal cavity 104. In the present embodiment, one or more stabilizing agents are also enclosed and positioned in the internal cavity 104 along with the phase change material to form a stabilized phase change composition 106. The hollow shell 102 may offer an additional degree of protection to the enclosed phase change material from oxidative or thermal degradation. For instance, the hollow shell 102 may reduce exposure of the enclosed phase change material to oxygen or oxygen free radicals. At the same time, a stabilizing agent that is positioned in the internal cavity 104 may provide oxidative or thermal stabilization not just to the enclosed phase change material but also to the hollow shell 102.

In general, the hollow shell 102 may be formed in a variety of regular or irregular shapes (e.g., spherical, ellipsoidal, and so forth) and sizes. According to some embodiments of the invention, the hollow shell 102 may have a maximum linear dimension (e.g., diameter) ranging from about 0.01 to about 2000 microns or from about 0.01 to about 500 microns. According to an embodiment of the invention, the hollow shell 102 is generally spherical and has a diameter that is less than about 100 microns (e.g., from about 0.5 to about 3 microns).

In the presently discussed embodiment, the hollow shell 102 comprises a base material 108. In general, the base material 108 may comprise any substance (or mixture of substances) that can be formed into the hollow shell 102. According to some embodiments of the invention, the base material 108 may be selected in accordance with one or more desired physical properties for the hollow shell 102. Exemplary desired physical properties

include, by way of example and not by limitation, mechanical properties (e.g., high strength, high hardness, high flexibility, or low porosity), thermal properties (e.g., high thermal stability), and chemical properties (e.g., low chemical reactivity with respect to the enclosed phase change material or enclosed stabilizing agent).

5 Exemplary base materials include, by way of example and not by limitation, fatty alcohols (e.g., natural and synthetic fatty alcohols), fatty acids, fatty esters, waxes (e.g., natural waxes, synthetic waxes, and modified waxes), polymeric materials (e.g., polyamides, polyamines, polyimides, polyacrylics, polycarbonates, polydienes, polyepoxides, polyesters, polyethers, polyflourocabons, formaldehyde polymers, natural polymers, polyolefins, polyphenylenes, silicon containing polymers, polyurethanes, polyvinyls, polyacetals, polyarylates, copolymers, and mixtures thereof), and mixtures thereof.

10 The phase change composition 106 may be encapsulated using a variety of methods to form the encapsulated phase change material 100. For instance, the phase change composition 106 may be provided as a particle (or particles) or droplet (or droplets), and the particle or droplet may be encapsulated via interfacial polymerization at an outer surface of the particle or droplet to form the hollow shell 102 enclosing the particle or droplet. As another example, the particle or droplet may be coated with a polymeric material in a liquid form (e.g., a molten form), and the polymeric material coating the particle or droplet may 15 then be cured to form the hollow shell 102 enclosing the particle or droplet. Further details regarding exemplary encapsulation methods are described in Tsuei et al., U.S. Patent No. 5,589,194, entitled "Method of Encapsulation and Microcapsules Produced Thereby"; Tsuei, et al., U.S. Patent No. 5,433,953, entitled "Microcapsules and Methods for Making Same"; Hatfield, U.S. Patent No. 4,708,812, entitled "Encapsulation of Phase Change 20 Materials"; and Chen et al., U.S. Patent No. 4,505,953, entitled "Method for Preparing Encapsulated Phase Change Materials", the disclosures of which are herein incorporated by reference in their entirety.

25 Once formed, stabilized encapsulated phase change materials (e.g., the encapsulated phase change material 100) may be used in melt spinning processes, extrusion processes, or injection molding processes to form a variety of articles having enhanced reversible thermal properties. According to some embodiments of the invention, the encapsulated phase change materials may be mixed with one or more polymeric materials to form a blend, and the resulting blend may then be processed to form, by way of example and not by limitation,

synthetic fibers (e.g., nylon fibers, polyester fibers, polyethylene fibers, polypropylene fibers, and multi-component fibers), films, foams, sheets, pellets, granules, rods, and injection molded articles. As discussed previously, one or more additional stabilizing agents may be added when forming the blend to provide additional oxidative or thermal stabilization to either or both the encapsulated phase change materials and the one or more polymeric materials. The one or more additional stabilizing agents may, for example, be dispersed in a melt of the one or more polymeric materials or may be added in a wet flushing step (e.g., to remove water, if present, coating or absorbed by the encapsulated phase change materials).

Turning next to FIG. 2, an enlarged cross sectional view of another exemplary embodiment of an encapsulated phase change material 200 is illustrated. As with the previously discussed embodiment, the encapsulated phase change material 200 comprises a hollow shell 202 defining an internal cavity 204, and a phase change material 206 is enclosed and positioned in the internal cavity 204.

In the present embodiment, the hollow shell 202 comprises a base material 208 that has one or more stabilizing agents 210 dispersed therein, and a stabilizing agent may be an antioxidant or a thermal stabilizer. Here, the base material 208 provides a matrix within which the one or more stabilizing agents 210 may be dispersed, and the base material 208 may be selected to be compatible with or to have an affinity for the one or more stabilizing agents 210. Exemplary base materials have been discussed previously. By dispersing a stabilizing agent within the base material 208, oxidative or thermal stabilization may be provided to either or both the hollow shell 202 and the enclosed phase change material 206.

The one or more stabilizing agents 210 may be homogeneously or uniformly dispersed within the base material 208. Alternatively, the one or more stabilizing agents 210 may be non-uniformly dispersed within the base material 208, such as, for example, to concentrate a stabilizing agent in one or more regions or layers of the base material 208 or to distribute the stabilizing agent in accordance with a concentration profile along one or more directions (e.g., a radial direction) along the base material 208. For instance, a stabilizing agent may be dispersed within the base material 208 such as to concentrate the stabilizing agent near an inner surface of the hollow shell 202. Such a configuration may provide greater contact between the stabilizing agent and the enclosed phase change material 206 to facilitate oxidative or thermal stabilization functions provided by the stabilizing agent. It should be recognized that, alternatively or in conjunction, one or more

stabilizing agents may be coated on an outer surface or an inner surface of the hollow shell 202.

The hollow shell 202 may comprise from about 0.01 percent to about 10 percent by weight of a stabilizing agent and from about 90 percent to about 99.99 percent by weight of the base material 208, according to some embodiments of the invention. According to an embodiment of the invention, the hollow shell 202 typically comprises from about 0.02 percent to about 1 percent by weight of a stabilizing agent.

It should be recognized that two or more stabilizing agents may be dispersed within the hollow shell 202, and the stabilizing agents may differ from each other in some fashion. For instance, the hollow shell 202 may have an antioxidant and a thermal stabilizer, two different antioxidants, or two different thermal stabilizers dispersed therein. According to some embodiments of the invention, the hollow shell 202 may comprise from about 0.01 percent to about 10 percent by weight and typically from about 0.02 percent to about 1 percent by weight of the two or more stabilizing agents taken collectively. According to other embodiments of the invention, the hollow shell 202 may comprise from about 0.01 percent to about 10 percent by weight and typically from about 0.02 percent to about 1 percent by weight of each of the two or more stabilizing agents.

It should be further recognized that one or more stabilizing agents may be enclosed and positioned in the internal cavity 204 along with the enclosed phase change material 206 to form a stabilized phase change composition. The one or more stabilizing agents comprising the enclosed phase change composition may be the same as or different from the one or more stabilizing agents 210 dispersed within the hollow shell 202. For instance, the hollow shell 202 may have an antioxidant dispersed therein, while a thermal stabilizer may be positioned in the internal cavity 204 along with the enclosed phase change material 206.

The encapsulated phase change material 200 may be formed using a variety of methods. For instance, a particle or droplet of the phase change material 206 may be encapsulated via interfacial polymerization in the presence of the one or more stabilizing agents 210 to form the hollow shell 202 having the one or more stabilizing agents 210 dispersed therein. As another example, the one or more stabilizing agents 210 may be dispersed in a polymeric material in a liquid form (e.g., a molten form) to form a blend, and the particle or droplet of the phase change material 206 may be coated with the blend, which may be subsequently cured to form the hollow shell 202. Once formed, encapsulated phase change materials (e.g., the encapsulated phase change material 200) may be used in melt

spinning processes, extrusion processes, or injection molding processes to form a variety of articles having enhanced reversible thermal properties. As discussed previously, one or more additional stabilizing agents may be used to provide additional oxidative or thermal stabilization.

5 Various other embodiments are within the spirit and scope of the invention. For instance, an embodiment of the invention relates to stabilizing a phase change material in a non-encapsulated form for melt spinning processes, extrusion processes, or injection molding processes. In the present embodiment, one or more stabilizing agents independently selected from the group consisting of antioxidants and thermal stabilizers may be separately provided and need not be mixed (e.g., pre-mixed) with the phase change material. The phase change material and the one or more stabilizing agents may be mixed with one or more polymeric materials to form a blend. It should be recognized that a variety of methods may be used to mix the phase change material, the one or more stabilizing agents, and the one or more polymeric materials. For instance, the one or more polymeric materials may be heated to form a melt, and the phase change material and the one or more stabilizing agents may be added to and dispersed in the melt to form the blend. The phase change material and the one or more stabilizing agents may be added at the same time or at different times. As another example, the phase change material, the one or more stabilizing agents, and the one or more polymeric materials may be provided together, heated, and mixed to form the blend (e.g., by feeding into an extruder). Once formed, the blend may be processed to form a variety of articles having enhanced reversible thermal properties. For instance, the blend may be melt spun to form synthetic fibers or may be extruded or injection molded to form sheets, films, foams, pellets, granules, rods, and so forth.

25 As another example, an embodiment of the invention relates to stabilizing a phase change material in an encapsulated form for melt spinning processes, extrusion processes, or injection molding processes. In the present embodiment, encapsulated phase change materials may be provided, wherein an encapsulated phase change material may comprise a hollow shell defining an internal cavity and a phase change material enclosed and positioned in the internal cavity. One or more stabilizing agents independently selected from the group consisting of antioxidants and thermal stabilizers may be separately provided, and the encapsulated phase change materials and the one or more stabilizing agents may be mixed with one or more polymeric materials to form a blend. A variety of

methods may be used to mix the encapsulated phase change materials, the one or more stabilizing agents, and the one or more polymeric materials. For instance, the one or more polymeric materials may be heated to form a melt, and the encapsulated phase change materials and the one or more stabilizing agents may be added to and dispersed in the melt to form the blend. The encapsulated phase change materials and the one or more stabilizing agents may be added at the same time or at different times. In particular, the one or more stabilizing agents may be added in a wet flushing step (e.g., to remove water, if present, coating or absorbed by the encapsulated phase change materials). As another example, the encapsulated phase change materials, the one or more stabilizing agents, and the one or more polymeric materials may be provided together, heated, and mixed to form the blend (e.g., by feeding into an extruder). Once formed, the blend may be processed to form a variety of articles having enhanced reversible thermal properties.

Each of the patent applications, patents, publications, and other published documents mentioned or referred to in this specification is herein incorporated by reference in its entirety, to the same extent as if each individual patent application, patent, publication, and other published document was specifically and individually indicated to be incorporated by reference.

While the present invention has been described with reference to the specific embodiments thereof, it should be understood by those skilled in the art that various changes may be made and equivalents may be substituted without departing from the true spirit and scope of the invention as defined by the appended claims. In addition, many modifications may be made to adapt a particular situation, material, composition of matter, method, process step or steps, to the objective, spirit and scope of the present invention. All such modifications are intended to be within the scope of the claims appended hereto. In particular, while the methods disclosed herein have been described with reference to particular steps performed in a particular order, it will be understood that these steps may be combined, sub-divided, or re-ordered to form an equivalent method without departing from the teachings of the present invention. Accordingly, unless specifically indicated herein, the order and grouping of the steps is not a limitation of the present invention.

What is claimed is:

1. A stabilized phase change composition comprising:
 - a phase change material; and
 - 5 a stabilizing agent selected from the group consisting of antioxidants and thermal stabilizers.
2. The phase change composition of claim 1, wherein the phase change material is selected from the group consisting of hydrocarbons, waxes, oils, fatty acids, fatty acid esters, dibasic acids, dibasic esters, 1-halides, primary alcohols, aromatic compounds, 10 stearic anhydride, ethylene carbonate, polyhydric alcohols, polymers, and mixtures thereof.
3. The phase change composition of claim 1, wherein the stabilizing agent is an antioxidant selected from the group consisting of phenolic antioxidants and thioether antioxidants.
4. The phase change composition of claim 1, wherein the stabilizing agent is a thermal 15 stabilizer selected from the group consisting of phosphites and phosphonites.
5. The phase change composition of claim 1, comprising from about 0.01 percent to about 10 percent by weight of the stabilizing agent.
6. The phase change composition of claim 1, comprising from about 0.02 percent to about 1 percent by weight of the stabilizing agent.
- 20 7. The phase change composition of claim 1, wherein the stabilizing agent is an antioxidant, and wherein the phase change composition further comprises a thermal stabilizer.
8. An encapsulated phase change material comprising:
 - a hollow shell defining an internal cavity; and
 - 25 a phase change composition positioned in the internal cavity, wherein the phase change composition comprises a phase change material and a stabilizing agent selected from the group consisting of antioxidants and thermal stabilizers.
9. The encapsulated phase change material of claim 8, wherein the hollow shell has a maximum linear dimension less than 100 microns.

10. The encapsulated phase change material of claim 8, wherein the phase change material is a hydrocarbon or a mixture of hydrocarbons.

11. The encapsulated phase change material of claim 8, wherein the stabilizing agent is a sterically hindered phenolic antioxidant.

5 12. The encapsulated phase change material of claim 8, wherein the stabilizing agent is a phosphite.

13. An encapsulated phase change material comprising:

10 a hollow shell defining an internal cavity, wherein the hollow shell comprises a base material and a stabilizing agent dispersed within the base material, and wherein the stabilizing agent is selected from the group consisting of antioxidants and thermal stabilizers; and

15 a phase change material positioned in the internal cavity.

14. The encapsulated phase change material of claim 13, wherein the stabilizing agent is an antioxidant selected from the group consisting of phenolic antioxidants and thioether antioxidants.

15. The encapsulated phase change material of claim 13, wherein the stabilizing agent is a thermal stabilizer selected from the group consisting of phosphites and phosphonites.

16. The encapsulated phase change material of claim 13, wherein the hollow shell comprises from about 0.01 percent to about 10 percent by weight of the stabilizing agent.

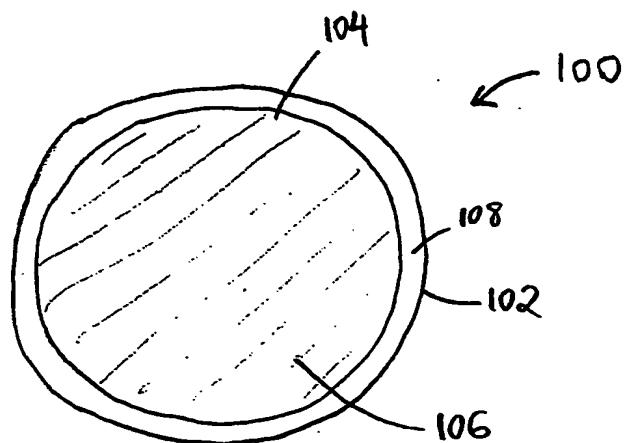
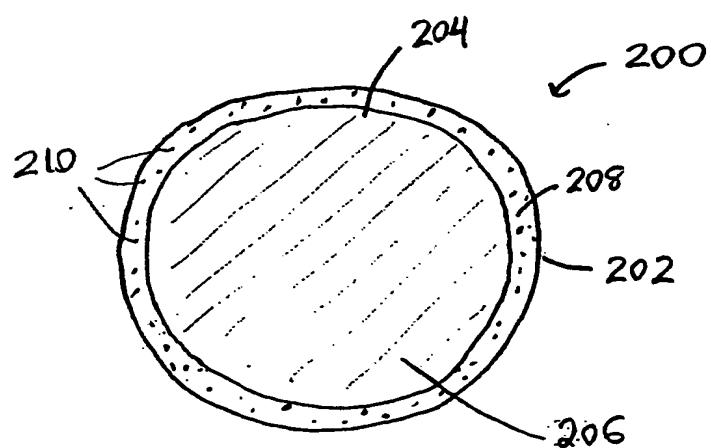
20 17. The encapsulated phase change material of claim 13, wherein the stabilizing agent is an antioxidant, and wherein the hollow shell further comprises a thermal stabilizer dispersed within the base material.

18. The encapsulated phase change material of claim 13, wherein the base material is a polymeric material.

25 19. The encapsulated phase change material of claim 13, wherein the phase change material is a hydrocarbon or a mixture of hydrocarbons.

20. The encapsulated phase change material of claim 13, wherein the stabilizing agent is a first stabilizing agent, wherein the encapsulated phase change material further comprises a second stabilizing agent positioned in the internal cavity, and wherein the second stabilizing agent is selected from the group consisting of antioxidants and thermal stabilizers.

1/1

**FIGURE 1****FIGURE 2**

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(54) Title: STABLE PHASE CHANGE MATERIALS FOR USE IN TEMPERATURE REGULATING SYNTHETIC FIBERS, FABRICS AND TEXTILES

(57) Abstract: A stabilized phase change composition comprises a phase change material and a stabilizing agent selected from the group consisting of antioxidants and thermal stabilizers. The stabilizing agent provides oxidative or thermal stabilizing to the phase change material. The stabilized phase change composition may be used or incorporated in a variety of process (e.g., melt spinning processes, extrusion processes, injection molding processes, and so forth) to form articles having enhanced reversible thermal properties. Exemplary articles that may be formed include, by way of example and not by limitation, synthetic fibers (e.g., nylon fibers, polyester fibers, polyethylene fibers, polypropylene fibers, and multi-component fibers), fabric materials, textiles, films, foams, sheets, pellets, granules, rods, and injection molded articles.

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 31081 A (HOECHST CELANESE CORP) 28 August 1997 (1997-08-28) page 5, line 22 -page 6, line 12 page 8 page 9 claims 1,2 -----	1-7
X	US 5 804 266 A (SALYER IVAL O) 8 September 1998 (1998-09-08) column 5, line 29 - line 40 examples -----	1-3,5,6 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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- *A* document defining the general state of the art which is not considered to be of particular relevance
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 199826 Derwent Publications Ltd., London, GB; Class E19, AN 1998-292400 XP002194302 & JP 10 102050 A (ASAHI DENKA KOGYO KK), 21 April 1998 (1998-04-21) abstract ---	1-3,5,6
X	DATABASE WPI Section Ch, Week 200024 Derwent Publications Ltd., London, GB; Class E14, AN 2000-281179 XP002194303 & RU 2 126 813 C (UNIV SAMARA), 27 February 1999 (1999-02-27) abstract ---	1-3,5,6
X	DATABASE WPI Section Ch, Week 198645 Derwent Publications Ltd., London, GB; Class E17, AN 1986-295816 XP002194304 & JP 61 218683 A (AGENCY OF IND SCI & TECHNOLOGY), 29 September 1986 (1986-09-29) abstract ---	1-3,5
X	DATABASE WPI Section Ch, Week 199408 Derwent Publications Ltd., London, GB; Class A97, AN 1994-062230 XP002194305 & JP 06 017042 A (MITSUBISHI CABLE IND LTD), 25 January 1994 (1994-01-25) abstract ---	1,2
X	HAN SEONGOK ET AL: "Thermal/oxidative degradation and stabilization of polyethylene glycol" POLYMER; POLYMER JAN 1997 ELSEVIER SCIENCE LTD, OXFORD, ENGL, vol. 38, no. 2, January 1997 (1997-01), pages 317-323, XP002194435 the whole document ---	1-3
X	DE 43 07 065 A (ST SPEICHERTECHNOLOGIE GMBH) 9 June 1994 (1994-06-09) column 5, line 15 - line 24 claims 1,26 ---	1-3
A	EP 0 306 202 A (TRIANGLE RES & DEV CORP) 8 March 1989 (1989-03-08) the whole document -----	1,8,13
1		

FURTHER INFORMATION CONTINUED FROM PCT/USA/ 210

Continuation of Box I.2

Present claims 1-20 relate to an extremely large number of possible stabilized phase change compositions comprising a phase change material and a stabilizing agent. Support within the meaning of Article 6 PCT and disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the compositions claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the compositions comprising either an antioxidant selected from the group consisting of phenolic antioxidants and thioether antioxidants or thermal stabilizers selected from the group consisting of phosphites or phosphonites (s. claims 3,4).

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte. n.ional Application No

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Patent document cited in search report		Publication date		Patent family member(s)		Publication date
WO 9731081	A	28-08-1997	US WO US	5709740 A 9731081 A1 5772949 A		20-01-1998 28-08-1997 30-06-1998
US 5804266	A	08-09-1998	AU AU EP JP NZ WO ZA	729444 B2 2589997 A 0902818 A1 10067981 A 331894 A 9735942 A1 9702455 A		01-02-2001 17-10-1997 24-03-1999 10-03-1998 29-07-1999 02-10-1997 29-09-1997
JP 10102050	A	21-04-1998		NONE		
RU 2126813	C	27-02-1999	RU	2126813 C1		27-02-1999
JP 61218683	A	29-09-1986	JP JP	1005636 B 1516089 C		31-01-1989 07-09-1989
JP 6017042	A	25-01-1994	JP	2779990 B2		23-07-1998
DE 4307065	A	09-06-1994	DE AT AU AU BR CA CN CZ DE DK WO EP ES FI HU JP NO NZ PL PT SK US ZA	4307065 A1 195966 T 682482 B2 5628994 A 9307568 A 2150918 A1 1089295 A , B 9501174 A3 59310095 D1 672095 T3 9412588 A1 0672095 A1 2149862 T3 952595 A 72270 A2 8509247 T 952155 A 258561 A 309256 A1 672095 T 63295 A3 6227285 B1 9309034 A		09-06-1994 15-09-2000 09-10-1997 22-06-1994 15-06-1999 09-06-1994 13-07-1994 13-12-1995 05-10-2000 02-01-2001 09-06-1994 20-09-1995 16-11-2000 29-05-1995 29-04-1996 01-10-1996 31-05-1995 27-05-1998 02-10-1995 31-01-2001 10-01-1996 08-05-2001 03-02-1995
EP 0306202	A	08-03-1989	US CA DE DE EP JP JP JP	4756958 A 1315083 A1 3854106 D1 3854106 T2 0306202 A2 1085374 A 1851056 C 5055607 B		12-07-1988 30-03-1993 10-08-1995 08-02-1996 08-03-1989 30-03-1989 21-06-1994 17-08-1993

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